

Alsberg-Schoch Memorial Lectureship

Opportunities and Challenges for New Industrial Uses of Starch¹

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Just eight years ago in 1986, Otto Wurzburg delivered the Alsberg-Schoch Memorial Award Address entitled "Forty Years of Industrial Starch Research" (1). Wurzburg traced the development of modified starches for industrial and food uses from the early work on the degradation of starch granules with acid, heat, or oxidants to the current generation of much more sophisticated starch derivatives. He recognized the efforts of many starch scientists who dedicated themselves to understand more about the structure of starch and its properties. This dedication to exploit starch and its inherent properties, to enhance its functionality, and to introduce new properties has allowed the markets for starch to increase in number, kind, and volume.

Today in the United States, nearly 5 billion lb of starch, recovered mostly from corn, is used in a variety of industrial applications. Although the primary application for starch is in the paper industry, which uses about 3.5 billion lb, it also is used in the textile industry and in several other industries as a flocculant, binder, adhesive, absorbant, or thickening agent and for chemical or biological conversion to chemicals. The market growth for starch during the last two or three decades is somewhat remarkable, considering that during this period, both public and private support for research on starch, especially industrial uses for starch, declined substantially.

I would like to be able to accurately

describe what can be expected in the growth of industrial uses and markets during the next 40 years. However, for me to attempt to do so would be folly, especially in view of the somewhat cyclical nature of the interest in this area over the last 40 years. It is possible to make some reasonable forecast of the future for industrial starch research by examining the forces that drive interest in this area. I will focus on forces behind the

Vast new markets for starch ... await development ...

current heightened interest in industrial starch research and look to the future for one of the industrial areas receiving considerable attention today.

After nearly 25 years of diminished support for research into new industrial uses for starch, now, in just the last few years, there has been a resurgence of interest in this topic. This has resulted in a dramatic increase in research activity in academia, the public sector, and industry. This high level of interest and activity is not confined to the United States but is rivaled in many foreign countries. The driving forces behind this resurgence appear to be strengthening, providing today what appears to be the greatest opportunity to develop new industrial uses for starch than any time during the last two or three decades. Vast new markets for starch and greater expansion of existing ones await development of a more thorough knowledge of starch science and technology.

CURRENT FORCES DRIVING INDUSTRIAL USES

What has led to the resurgence of interest in starch? What are the driving

forces behind this resurgence? Is there reasonable assurance that this interest will continue to have broad support? These are valid questions to be asked, especially by those who have had long-standing interest in industrial uses for starch. We need to have answers to these questions for the starch scientist to assess how real and how substantial the opportunity is to conduct research and development activities in this area.

From the perspective of one who has been interested in starch science and technology for more than 30 years, during which time broad support mostly declined, it appears that the heightened interest can be traced to several somewhat unrelated events occurring over the last few years. During the mid-1980s, at a time when there was increasing taxpayer concern over the amount of subsidies paid to farmers, the amount of corn produced in the United States exceeded markets for this grain by more than 4 billion bushels in each of the years 1985-1987. This unprecedented surplus, representing about one-half of the year's crop, resulted in increased research activity in the federal sector and in federal support of research in academia. State governments, especially in those states with substantial corn production, also began providing funding to their local colleges and universities for research that might lead to new uses for corn.

Because the outlook for increased foreign markets for our grain was less than encouraging, due mostly to competition from countries that once were importers and now are exporters of cereal grains, the search for new markets received broader support. Commodity groups representing corn interests intensified efforts to encourage more research and development activities. So too did groups with an interest in promoting wheat. This activity was highly focused toward the development of technology that would lead to new uses and new industrial products. Because starch comprises more than 60% of the composition of the cereal grains, much of the research activity was directed toward the starch component.

Today, the U.S. Departments of Agriculture, Defense, and Energy provide

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considerable grant funds in support of research and development efforts into industrial uses for corn and other agriculture and forest products. Commodity organizations, both at the state and national levels, are providing funding for specific product development efforts and are lobbying legislative bodies to increase the level of funding in these areas. Agriculture and forest products are seen as a vast resource of renewable raw material for industry to reduce dependence on imports and to provide more environmentally benign alternatives to many current industrial products now derived from petroleum (2). Moreover, fully exploiting what we are capable of producing on our land by processing more of the raw commodities into products with added value is seen as a stimulus to rural and urban sectors through new and expanded industries, a boost to the economy through higher value products for both domestic and export markets, and an opportunity to reduce subsidy payments.

The 1980s also witnessed a worldwide heightening of concern over problems associated with the handling and disposal of solid waste. The almost unmanageable volume of solid waste generated and the forecast of ever-increasing amounts caused many nations to evaluate the waste being generated and to develop methods to reduce the amount of waste. Disposal of waste by burying became problematic as landfills were being overburdened and space for additional landfills was dwindling. Analysis of waste going to landfill identified that from 17 to 25% of the volume of the landfill was being occupied by discarded plastics, especially those that were used one time and disposed of. Of the 16 billion lb of plastics used for packaging, much ends up in landfills after one-time use. From these findings, support emerged for development of plastics based on natural products as biodegradable alternatives to many of those derived from petroleum. Starch received immediate attention as one of the most favorable materials from which to develop the biodegradable alternatives.

Although opposition by certain factions to the development of alternatives to existing plastics led to considerable debate, often because of misunderstandings of what could and could not be expected of biodegradable plastics, consumer interest in more environmentally "friendly" products spurred activity in developing starch-based plastics. Lack of clear understanding of biodegradability as applied to these new materials, although causing somewhat of a setback in early developments, resulted in a heightened awareness of opportunities for biodegradable materials and subsequently led to international efforts to develop standards for them.

The growing trend toward composting (especially of yard waste) also supports

efforts to develop plastics that are compostable. Composting was seen as a viable route to reduce the amount of solid waste going to landfills. There has been an almost five-fold increase in composting centers in the United States over the last five years to a total of nearly 3,000 today. Companies developing starch-based plastics have seized the opportunity to produce composting bags to replace those made from petrochemicals, because nonbiodegradable bags are not accepted at compost facilities. Fast food restaurants are participating with research organizations and companies developing biodegradable plastics in

composting studies of the waste collected from restaurants. Again, standards are being developed to define compostable material, and these are seen as enhancing the opportunity to develop acceptable alternatives to existing plastics.

Interest in and support for research on starch also has been increased by implementation of the Federal Technology Transfer Act of 1986 (Public Law 99-502) and by the Food, Trade, and Conservation Act of 1990 (Public Law 101-624). Both of these encourage close cooperation between the public and private sector in joint effort to develop and commercialize new technology. The

1986 act established Cooperative Research and Development Agreements (CRADAs) that greatly enhance and facilitate a close working relationship between the public sector and industrial firms. The Agricultural Research Service has entered into nearly 400 CRADAs since enactment of the legislation in 1987. At the National Center for Agricultural Utilization Research (NCAUR), several CRADAs have been entered into with companies where there is mutual interest in developing industrial products from starch.

The 1990 act, referred to as the 1990 Farm Bill, authorized the Alternative Agriculture Research and Commercialization (AARC) Center to facilitate and enhance development and commercialization of industrial products manufactured from farm and forestry materials. In 1993, the AARC Center funded about 26 projects for a total expenditure of approximately \$10 million. Some of the projects fund development of starch technology. The Center's target was to fund up to \$20 million in FY94 and even larger amounts in succeeding years. The New Uses Council, a nonprofit organization established in 1990 to "develop and promote the use of renewable resources in the production of new nonfood industrial and consumer products," has urged

Congress to increase funding for AARC to as much as \$1 billion.

Thus, the driving forces to more fully develop our agricultural resources to reduce subsidy payments, improve our economy by processing more raw commodities into products with higher value for domestic and export markets, reduce dependence on imported petroleum, and provide more environmentally acceptable processes and products are quite strong and appear likely to remain so well into the future. Because cereal grains will continue to play an important role in providing food, feed, and industrial material and we have the ability to produce even more well beyond that required to meet food and feed needs, the future appears exceptionally bright for the opportunity to develop new uses and new industrial products from starch. The starch scientist and technologist must meet the challenges of conducting the basic and applied research required for a more thorough understanding of structure/functional property relationships, identifying the specific performance required of products to capture new markets, and developing new and more efficient physical, chemical, and biological conversion technologies that will lead to the desired product with optimal properties.

The increased activity to expand current industrial markets for starch and to develop new products and capture new markets is quite broad. Developing new and improved products for the paper industry continues to allow expansion of markets for starch in this industry (3). Conversion of starch into chemicals as direct replacements for, or as alternatives to, many of those produced from petroleum is receiving increased attention (2). New organisms are being identified, or current ones genetically altered, to enhance efficiency of starch fermentations. Conversion of starch into other biopolymers through microbial/enzymatic conversions has newfound interest in the search for more environmentally acceptable replacements for specific petroleum-derived polymers. A greater multidisciplinary effort is required to fully exploit the potential offered by biotechnological approaches to the discovery, characterization, modification and design of new enzyme/microbial systems that can effect desired conversions of starch. Coextrusion of starch at low moisture content with other polymers, especially ones that are biodegradable, to produce films, foams, and solid articles as totally biodegradable replacements for petroleum-based plastics is being studied in many laboratories.

DEVELOPMENT OF STARCH-BASED PLASTICS

While each of these research areas presents an excellent opportunity for expansion of industrial uses of starch, it is the area of starch-based plastics that has seen the most remarkable growth in activity during just the last few years. Since 1990, new national and international societies have been formed to promote research and development of biodegradable polymers and plastics. Meetings and conferences on this topic, both here and abroad, appear to be increasing at an almost exponential rate. And now, a nascent industry with the desire to produce a broad range of biodegradable plastic items to meet consumer demands for plastics that are more environmentally acceptable is emerging. The success of this industry will depend to a large degree on the ability of the starch scientist/technologist to meet the challenge to develop a fuller understanding of starch structure/functional property relationships, the interaction of starch with other polymers and additives, and the modifications of starch that can be effected under various processing conditions.

Our research group at NCAUR has had a long-standing interest in starch

chemistry and technology, especially with the goal of developing new uses and new industrial products from starch (4). For many years now, we have committed considerable effort to research and development of starch-based plastics. Rather than review all of our activities in this area, I will take a brief look at some of our efforts that were significant in laying part of the foundation for this area, which witnesses such a high level of activity today. A recent publication provides more of a historical look at the development of starch-based plastics (5).

One might trace the genesis of the nascent starch-based plastics industry to activity in the early 1970s in the United States and the United Kingdom. In response to the need for a biodegradable agricultural mulch film to obviate need for removal and disposal of the film at the end of a growing season, Otey and coworkers (6) at NCAUR developed starch-poly(vinyl alcohol) films and laminated them with poly(vinyl chloride) or plastic wrap to reduce water sensitivity. While these films exhibited properties satisfactory for mulch film, their cost was prohibitively high. This led to the development of films made first from starch and poly(ethylene-co-acrylic acid) (EAA), and then from starch, EAA, and polyethylene by Otey and coworkers (7). The films were made by extrusion blow-

ing from the polymer melt formed in the extruder. This technology, patented in the early 1980s, is used commercially today, perhaps with some modification, to prepare agricultural mulch film.

Granular Starch in Plastics

At about the same time that this research was in progress at NCAUR, work in the United Kingdom resulted in polyethylene films with incorporated starch granules, especially to improve the "hand feel" of shopping bags (8). This technology, commercialized in Europe in the 1970s, is characterized by using starch granules that have been dried to <1% moisture and then surface-treated to increase the compatibility of hydrophilic starch with hydrophobic polyolefin. The use of whole starch granules limits the amount of starch that is incorporated to around 10%. Incorporation of other additives, such as pro-oxidants, promotes degradation of the synthetic polymer. Today, in the United States, this technology and variants of it are used by Ecostar International (Tonawanda, NY) for the production of compost and trash bags, bottles, films and foams for packaging, and plastic cups, plates, and utensils, among other items.

In the early 1990s, Fully Compounded Plastics (Decatur, IL) began producing granular starch masterbatches for the production of mulch films, geotextiles, and molded articles. The masterbatches consist of starch and copolymers of ethylene and acrylic esters, such as poly(ethylene-co-methyl acrylate), poly(ethylene-co-ethylacrylate), and poly(ethylene-co-vinyl acetate) (9). This technology eliminates the need to surface-treat the starch, because the polar copolymers act as surfactants to lower the interfacial energy between the starch and polyolefin. In addition, by processing the material on a vented twin-screw extruder, the need to use dried starch is circumvented.

Thermoplastic Starch in Plastics

While markets for plastics with granular starch incorporated as a filler continue to grow, the greatest market penetration has occurred for technology where the starch granules have been totally disrupted. In the previously mentioned efforts of Otey and coworkers, the starch and synthetic polymers were processed in an extruder under conditions where the starch and the synthetic polymers became a melt that was processed into film through a blown film die on the extruder. Extrusion processing of starch under relatively low moisture conditions, both in the presence and absence of other polymers, has received considerable attention during the last few years and has resulted in new commercial ventures to manufacture starch-based biodegradable plastics (10).

The Novon Division of Warner-Lambert Company (Morris Plains, NJ) completed construction of a plant in Illinois in 1992 with the capacity to produce 100 million lb of starch-based plastic resins annually. Novon now produces five specialty grades of resin for extrusion processing into foam for packaging; injection molding into cutlery, golf tees, and medical disposables; cast and blown film into lawn and leaf compost bags; and blow-molding into bottles and other containers.

The Novon Division was formed in 1990 after research on extrusion of starch and gelatin to form capsules for pharmaceuticals (11). During these studies, the workers observed that starch became thermoplastic when treated under certain conditions in the extruder or during injection molding. The term "destructured" was coined to describe the starch extrudate formed by treatment of starch containing 5-30% moisture at elevated pressure and at a temperature above its glass transition and melting temperatures. Injection molding of starch under similar conditions also gave the starch melt. A later patent issued to Warner-Lambert Company describes several thermoplastic compositions containing "destructured" starch and various other polymers (12) that form the basis of the starch-based resins now being manufactured.

Several starch-based resins, under the name Mater-Bi, are being produced and marketed by Novamont, a company belonging to the Ferruzzi-Montedison Group of Italy. Novamont was formed in 1989 to develop industrial products from agricultural raw materials that would be more environmentally compatible than many nonbiodegradable products currently being used. The Mater-Bi resins are produced in several grades for injection and blow molding, sheet extrusion and thermoforming, and blown and cast film. Several commercial products are produced from these resins including cutlery, typewriter cartridges, pen barrels, cosmetic boxes, disposable razors, shopping, trash and compost bags, cotton swabs, drinking straws, nursery pots, and containers for dry powders and oils.

The various grades of Mater-Bi resins contain from 60 to 75% natural material such as cornstarch and up to 40% of a synthetic polymer such as poly(vinyl alcohol), poly(ethylene-co-acrylic acid), poly(ethylene-co-vinyl alcohol), or poly(vinyl acetate) (13). The resins are prepared by extrusion under conditions where the starch and synthetic polymer form a thermoplastic melt and are described to have an interpenetrating network of the polymer components. Extensive biodegradation studies have been conducted with the resins and articles made from them.

A foam loose-fill packing material consisting of 95% starch was introduced four years ago by American Excelsior

Company (Arlington, TX) as an alternative to polystyrene loose fill. Developed by National Starch and Chemical Company (Bridgeport, NJ) and trademarked Eco-Foam, the material is prepared from a slightly hydroxypropylated high-amylose cornstarch by extrusion in a temperature range of 160–250°C (14). A small percentage of poly(vinyl alcohol) is coextruded with the starch in the presence of about 16% moisture. Foam made from starch containing 70% apparent amylose has resiliency and compressibility properties similar to those of polystyrene foam (15). Although the starch foam has good shelf life even at high humidity, it rapidly dissolves in water and completely biodegrades in soil.

Gelatinized Starch in Plastics

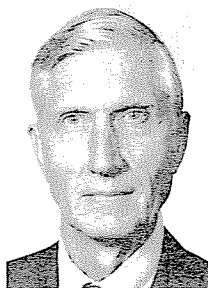
About four years ago, the Franz Haas Waffelmaschinen Company (Vienna, Austria), a manufacturer of machinery and equipment for producing molded sugar cones, cream filled wafers, waffles, etc., began a new venture called Biopac Biological Packing Systems. Under the name Biopac, they now are producing a variety of starch-based foam items intended for one-time use and then disposal (16). Items include fast food service items such as cups, trays, sandwich containers, french fry holders, and plates. Also, they produce blisters and trays for

confectionery goods. Many items are already approved for food packaging uses in some European countries.

Biopac is made from starch, plant fibers, and food additives. Articles can consist of 100% starch, but plant fiber and plasticizers may be added to improve physical properties. For improved moisture stability, the company has developed coatings. Unlike the technology described previously, the Biopac technology involves feeding an aqueous starch mass into a mold, heating (baking), and evaporating the water. As might be expected, articles made by this technology are completely biodegradable.

Biopolymer Plastics

While the technologies described utilize starch mostly in its native polymeric form, biopolymers that either are or could be produced from starch through microbial/enzymatic conversions are receiving considerable attention as biodegradable plastics. For two of these, poly(lactic acid) (PLA) and poly(hydroxy butyrate-co-hydroxy valerate) (PHBV), new commercial ventures have recently been formed. In 1992, Ecochem, a joint venture of ConAgra and DuPont, and Cargill, Inc., announced new ventures to produce PLA and develop applications as alternatives to nonbiodegrad-



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able plastics. In this same year, ICI Biological Products (now Zeneca Biological Products) introduced shampoo bottles made from PHBV in the United States. For both of these biopolymers, cost is a major concern, and considerable effort will be devoted to improving the efficiency of fermentation and recovery processes. Another approach to lower cost, one that provides a good challenge to the scientist, is the coextrusion of the biopolymer with starch. Several researchers are studying composites and interpenetrating networks that can be formed on coprocessing of such mixtures. Currently, we are pursuing development of starch-PHBV compositions under a CRADA with Zeneca Biological Products.

For the nascent biodegradable plastics industry to not only survive but also to thrive and capture an increasing share of the potential multi-billion pound market for alternatives to nonbiodegradable plastics, current research and development efforts must be expanded. We must have a better understanding of the relationship of starch composition and structure with functional properties. This understanding will permit the chemist/engineer to design modifications to enhance properties and assist the geneticist/biotechnologist to introduce appropriate structural changes in the starch molecule in the growing plant. We must continue to expand on the knowledge of the behavior of starch during extrusion processing and to define processing parameters to effect desired modifications. Starch-water relationships as they impact transitions and flow properties of starch during extrusion must be further characterized. Better approaches are needed to improve the compatibility of starch with other polymers to enhance performance of these mixed polymer systems. The change in physical properties of starch-based plastics with time due to moisture sensitivity and embrittlement must be overcome. These are just some of the areas requiring attention by the researcher.

CONCLUSIONS

For the starch scientist/technologist, this is an opportunistic period. Today, there exist several interests and concerns that provide the exceptional opportunity for development of industrial products from starch. Concern for a better environment and interest in products that are more environmentally benign, interest in renewable resources and more efficient use of our agricultural products, and the need to process more of what we produce into products of higher value for domestic and export markets are driving forces that provide an opportunity to develop new uses for starch. We must seize this opportunity and meet the challenges facing us. Resolution of the scientific/

technological problems confronted in just one area alone, starch-based plastics, could result in a vibrant industry and provide a new multi-billion pound market for starch.

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